Electrochimica Acta 54 (2009) 1777–1783

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

A study of iodine adlayers on polycrystalline gold electrodes by *in situ* electrochemical Rutherford backscattering (ECRBS)

Adrian Hightower[a,*,1], Bruce Koel[b], Thomas Felter[c]

[a] Department of Physics, Occidental College, 1600 Campus Road, Los Angeles, CA 90041, United States
[b] Department of Chemistry, Lehigh University, 6 E. Packer Ave., Bethlehem, PA 18015, United States
[c] Hydrogen and Metallurgy Sciences, Sandia National Laboratory, 7011 East Avenue, Livermore, CA 94550, United States

ARTICLE INFO

Article history:
Received 31 December 2007
Received in revised form 4 October 2008
Accepted 4 October 2008
Available online 1 November 2008

Keywords:
Polycrystalline gold electrode
Iodine adsorption
In situ RBS
Ion scattering
Gold
Etching

ABSTRACT

Iodine adsorption on a polycrystalline gold electrode was studied by *in situ* electrochemical Rutherford backscattering (ECRBS) using an ultrahigh vacuum (UHV)-electrochemical cell comprising of a thin-film silicon nitride window. The depth resolution of RBS allowed for measurement of nuclide concentration of the diffuse double-layer, electrode surface and near-surface regions. ECRBS measurements on the gold electrode, initially exposed to −500 mV vs. a platinum pseudo-reference electrode, in a potassium iodide solution, showed an increase in the 2.07 MeV iodine peak indicative of iodine adsorption. The surface concentration of the iodine adlayer was directly measured by ECRBS to be $1.3 \pm 0.3\,\mathrm{nmol/cm^2}$. ECRBS measurements on a gold electrode exposed to 1.5 V vs. a platinum pseudo-reference electrode, in a potassium iodide solution display a decrease in the 2.16 MeV gold peak and a shift to lower energies. Scanning electron microscopy images of electrodes studied by ECRBS displayed roughened surfaces consistent with gold dissolution. This work demonstrates the potential for *in situ* ECRBS using thin-film silicon nitride windows to become a powerful tool for the investigation of a wide range of electrochemical processes in areas such as corrosion, electrodeposition and electrocatalysis.

1. Introduction

The results of *in situ* electrochemical Rutherford backscattering (ECRBS) measurements of iodine adlayers on polycrystalline gold electrodes are reported in this work. Historically, it has been extremely challenging to design *in situ* spectroscopy experiments that directly measure the electrode composition under potentiodynamic control due to the liquid nature of the electrode environment. Such measurements are essential for correlating electrode performance to dynamic nanostructures at the electrode surface and the composition of the electrical double-layer. The advent of numerous *in situ* electrochemical diffraction and spectroscopy techniques has greatly expanded our understanding of the electrode–electrolyte interface (EEI). However, until recently the direct measurement of elemental surface composition could only be accomplished with techniques functioning in ultrahigh vacuum (UHV) environments [1–3]. This has limited direct elemental measurements of the EEI to a variety of *ex situ* experiments.

In contrast to other *in situ* electrochemical diffraction or spectroscopy techniques, ECRBS provides quantitative elemental analysis of the EEI. The *in situ* electrochemical techniques of Fourier transform infrared spectroscopy (ECFTIR) [4–6], scanning tunneling microscopy (ECSTM) [7–9], and surface X-ray diffraction (ECSXS) [10,11] provide information on bonding, topography, and crystalline phases at the EEI, respectively. As a complement to the aforementioned techniques, ECRBS is a rapid, non-destructive technique that measures the energy and intensity of backscattered ions whose energies are principally determined by the depth and the atomic number of the scattering center. Quantitative compositional analysis with an accuracy of up to 1% is enabled with RBS measurements by the fact that the number of scattered ions directly correlates to the number of scattering centers in the target [12]. When this technique is applied to a thin-film electrode deposited on a silicon nitride window separating the liquid and UHV environment, a compositional depth profile of the electrode and electrolyte can be obtained. ECRBS can probe large areas of the EEI under dynamic potential control. Currently, the analysis area for a given ECRBS measurement is $\sim 0.25\,\mathrm{mm^2}$ and is primarily dictated by the area of the UHV window. The probe depth of the RBS ion beam allows observation of the EEI through a thin-film electrode window assembly (~150 nm in thickness). The depth resolution of RBS (1–10 nm)

---

[*] Corresponding author. Tel.: +1 323 259 2826; fax: +1 323 341 4858.
E-mail address: hightower@oxy.edu (A. Hightower).
[1] SE member.

0013-4686/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2008.10.027

[13] allows for measurement of nuclide concentration of the diffuse double-layer, surface and near-surface layers.

Ion beam techniques have been applied previously to investigate liquid–solid interfaces with reasonable success [14,15]. These *in situ* studies avoided the problem of sample corruption associated with transferring between liquid and vacuum environments. Morita et al. [16] studied lead desorption from SiO_2 with RBS using a liquid cell equipped with a 3-mm diameter, 5 μm thick Si window. In this case, a 9-MeV $^4He^{2+}$, 0.6-mm diameter beam at an ion flux of $1.9 \times 10^{13}/cm^2$ s was able to resolve Xe gas at atmospheric pressure as well as a 4-monolayer Pd thin film in separate experiments. This work was complicated by the use of a 5-μm thick Si window that significantly reduced the intensity and energy of the Pd peak. Penetrating this window necessitated the use of high-energy ion beams and leads to spectra complicated by increased inelastic scattering. More recently, Bouquillon et al. [17] used a liquid cell to perform PIXE analysis on lead-containing aqueous solutions. Pb at concentrations less than 10 ppm were resolved using a 3-MeV proton beam at ~1 nA through a 100 nm Si_3N_4 window. This work also identified bubble formation at regions of beam impact attributed to water radiolysis. It was determined that these bubbles could be eliminated with sufficient circulation of the solution. Lastly, RBS studies of the near surface region of aqueous sulfuric acid solutions and HCl-doped ice were carried out using analysis chambers employing differential pumping apertures [18].

ECRBS measurements were first demonstrated by Kötz et al. to study copper deposition on iridium and oxide formation on titanium [19]. This pioneering work utilized 3 MeV and 2.5 MeV $^4He^+$ beams through a 1.2-μm thick Si window along with iridium and titanium working electrodes, platinum counter electrodes and palladium pseudo electrodes. A number of challenges in ECRBS measurements were identified including the overlap of signals from low atomic number scattering centers situated closer to the beam source with signals from higher atomic number scattering centers situated further from the beam source. The loss of depth resolution due to peak broadening as scattered ions traversed the electrode and cell window was another challenge. It is important to note that the thickness of the window separating the electrochemical and vacuum environments plays a critical role on the impact of signal overlap and loss of depth resolution. Subsequent ECRBS studies have employed windows ranging in thickness from ~1 μm to study Cu, Ag and Pd deposition on Si [20] to 3.5 μm to study deuterium ingress into Zr–2.5 wt.% Nb [21]. The current study utilizes a much thinner 150-nm thick Si_3N_4 window in the hopes of minimizing the influences of signal overlap and the loss of depth resolution.

Adsorption of aqueous iodine on a polycrystalline gold electrode served as a benchmark in testing the current ECRBS system. The adsorption of ordered-monolayer phases of iodine on gold electrodes has been studied extensively by cyclic voltammetry [22–24], surface X-ray scattering (SXS) [25,26], STM [8,27–31], and electrochemical quartz crystal microbalance (ECQCM) [32,33] techniques. Iodine adlayers on single crystal gold surfaces demonstrate potential-dependent phase transitions [31,34] and are known to have a strong impact on the underpotential deposition of metal ions [30,35]. Iodide solutions are known to be an effective alternative to cyanide in both the chemical [36] and electrochemical [37] etching of gold. In these processes, electrons are removed from the metallic gold and the subsequent gold ions form strong complexes with iodide in solution.

$$Au^+_{(aq)} + 2I^-_{(aq)} \leftrightarrow AuI^-_{2(aq)} \tag{1}$$

Iodine and gold atoms provide scattering centers with large nuclear masses and thus, larger RBS signals as predicted by the formula for differential scattering cross-sections:

$$\frac{\partial\sigma}{\partial\Omega} = \left[\frac{Z_1 Z_2 e^2}{4E}\right]^2 \cdot \frac{4}{\sin^4\theta} \cdot \frac{\left[\sqrt{1-(A\sin\theta)^2} - \cos\theta\right]^2}{\sqrt{1-(A\sin\theta)^2}} \tag{2}$$

The differential scattering cross-section represents the probability of a scattering event with solid angle, Ω, to occur as a function of the atomic numbers of the incident and target ions, Z_1 and Z_2; the energy of the incident ion, E; the angle of incidence, θ; and the mass ratio of the incident ions to the target atoms, A. This work utilizes 2.3 MeV He^+ ions ($Z_1 = 4$) to investigate the adsorption of iodine ($Z_2 = 53$) and etching of gold ($Z_2 = 79$).

We seek to demonstrate the capabilities of ECRBS using a 150-nm thick Si_3N_4 window for elemental characterization of electrochemical interfaces by measuring iodine adsorption on a polycrystalline gold electrode as well as etching of a gold electrode.

2. Experimental

Fig. 1a displays a sealed, UHV-electrochemical cell with a 1.5-mL liquid-filled-well that was fabricated from a vacuum-grade epoxy resin (Torr Seal®) and a 0.25-mm², 150-nm thick Si_3N_4 window. This UHV-electrochemical cell was placed directly inside the RBS

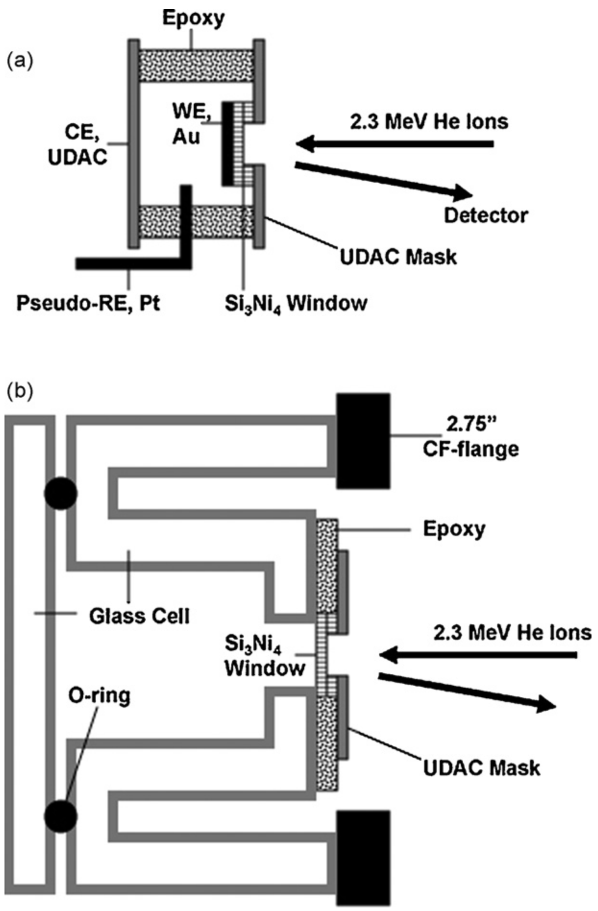

Fig. 1. (a) Schematic drawing of the UHV-electrochemical cell used in the ECRBS study of Au dissolution and I adsorption on a polycrystalline Au electrode. The cell incorporates a 0.25-mm² UDAC mask; a 0.25-mm², 150-nm thick Si_3N_4 window; a 10-nm thick Au working electrode (WE), a 125-μm diameter Pt wire to act as a pseudo-reference electrode (RE), a UDAC counter electrode (CE), and a sealed 1.5-mL liquid well. (b) Schematic drawing of the UHV-liquid cell used to test window stability. The cell incorporates a 0.25-mm² UDAC mask with a 0.25-mm², 500-nm thick Si_3N_4 window.